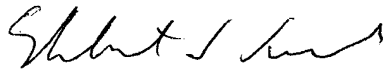


REMARKS

By way of the foregoing amendments to the claims, Claims 1-13 have been amended to delete the multiple dependencies and reference numerals. These changes have been made in accordance with 37 C.F.R. § 1.121 as amended on November 7, 2000. Marked-up versions of Claims 1-13 indicating the changes accompany this Preliminary Amendment. The Applicant requests early and favorable consideration with respect to this application. Should any questions arise in connection with this application, the undersigned respectfully requests that he be contacted at the number indicated below.

Respectfully submitted,

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Date: May 10, 2002

Attachment to Preliminary Amendment dated May 10, 2002

Marked-up Claims 1-13

1. (Amended) Method to produce a solar cell wherein on a substrate [(7)] a dissolvable intermediate layer [(6)] is deposited, on the intermediate layer [(6)] a layer structure [(11)] is deposited, the intermediate layer [(6)] is dissolved subsequently, which separates the layer structure [(11)] from the substrate [(7)], and thereby from the layer structure [(11)] a flexible solar cell is formed.
2. (Amended) Method according to claim 1 wherein the layer structure [(11)] is formed by a supporting layer [(5)] and a layer stack [(10)].
3. (Amended) Method according to claim 1 wherein the layer structure [(11)] is formed by a layer stack [(10)] and that after dissolution of the intermediate layer [(6)] the layer stack [(10)] is provided with a supporting layer [(5)].
4. (Amended) Method according to [one of claims 1-3] claim 1 wherein after dissolution of the intermediate layer [(6)] the substrate [(7)] is reused.
5. (Amended) Method according to [one of claims 1-4] claim 1 wherein the intermediate layer [(6)] consists of a material of the group of the alkali-halogenides like NaCl, KCl, NaF or of the group of the IIa-fluorides like BaF₂.

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Marked-up Claims 1-13

6. (Amended) Method according to [one of claims 1-5] claim 1 wherein several combinations of layer stacks [(10)] with or without separating layers between the layer stacks are deposited one upon the other.
7. (Amended) Application of the method according to [one of claims 1-6] claim 1 to produce energy on earth and in space and for consumer applications like pocket calculators and "smart cards".
8. (Amended) Solar cell according to [one of claims 1-7] claim 1 consisting of at least one absorber layer [(1)] of a semiconductor, of at least one window layer [(2)] of a semiconductor to couple the light in, of at least one at least partially transparent front contact [(3)] and at least one backcontact [(4)], wherein the solar cell contains at least one thin supporting layer [(5)] and that this supporting layer adjoins to the back contact [(4)] or is located on the front contact [(3)].
9. (Amended) Solar cell according to claim 8 wherein the supporting layer [(5)] consists of a plastic, preferably a polyimide, or of a metal or ceramic, and that its thickness is 1 - 100 μm , preferably 20 μm .

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Marked-up Claims 1-13

10. (Amended) Solar cell according to claim 8 [or 9] wherein the absorber layer [(1)] consists of a material of the group of I-III-VI compounds of the periodic system, like CuIn_xSe_y , $\text{CuIn}_x\text{Ga}_y\text{Se}_z$, $\text{CuIn}_x\text{Ga}_y\text{S}_z\text{Se}_u$, with $x, y, z, u \geq 0$, or of the II-VI compounds of the periodic system like CdTe, or III-V compounds of the periodic system like $\text{Al}_{1-x-y}\text{Ga}_x\text{In}_y\text{As}_{1-u-w}\text{P}_u\text{N}_w$ with $0 \leq x, y, u, w \leq 1$ or of group IV elements of the periodic system like Si or Ge.

11. (Amended) Solar cell according to [one of claims 8-10] claim 8 wherein the window layer [(2)] consists of a semiconductor material with a band gap which is at least as large as that of the absorber layer [(1)], and where the structure of the layers is polycrystalline or amorphous.

12. (Amended) Solar cell according to [one of claims 8-11] claim 8 wherein the absorber layer [(1)] consists of $\text{CuIn}_x\text{Ga}_y\text{S}_z\text{Se}_u$ with $x, y, z, u \geq 0$ and the window layer [(2)] contains at least one material of the group of doped or undoped ZnO, InSnO (ITO), CdS and ZnSe.

13. (Amended) Solar cell according to [one of claims 8-12] claim 8 wherein the flexible solar cell structure, depending on application, contains a rigid supporting material like glass, metal or ceramic.

-1-

~~{Flexible Un-layer solar cell~~~~}[Field of the Invention~~

[0001] The invention relates to a method for producing solar cells, as well as to a solar cell consisting of thin films only and which is flexible, according to patent claims 1 and 8..

[Background of the Invention

[0002] Flexible solar cells known up to now were manufactured ~~{directely}~~ [directly] onto metal foils or polymer foils. If polymer foils are used, compatibility problems arise between the polymer and the proper solar cell structure because of the limited temperature stability of polymers.

[[0003]] In addition, because of this limited temperature stability and inhomogenous stress distributions in the foils, unsuited surfaces may result, and, if the electrically active layers are fabricated by vacuum deposition techniques, local surface faults at the surface may lead to catastrophic electrical shorts in the finished cells. If metal foils are employed, the roughness of the foil surfaces may lead to problems (B.M. Basol et al. 25th IEEE Photovoltaic Specialist Conf. 1988, IEEE Service Center, New York, USA, 1996, pp. 157-162; M.A. Contreras et al., "Fabrication methods of Cu(In,Ga)Se₂ ~~{PO'YCrystalline}~~ [polycrystalline] materials and devices currently under development at the national renewable energy laboratory", Proc. 14th European Photovoltaic Solar Energy Conference, Barcelona, Spain, 1997, H.S. Stephens & Associates, UK, 1997, pp. 2354-2358).

[Summary of the Invention

[0004] It is the purpose of the present invention to describe a method to produce solar cells where a dissolvable intermediate layer allows the separation of the solar cell from a rigid substrate. An additional purpose is to propose a solar cell which consists of thin layers only and which is flexible.

[Brief Description of the Drawings]

[0005] According to the invention, these purposes are solved with a method according to the text of patent claim {1} [1] and with a solar cell according to the text of patent claim 8. In the following, the invention is described with reference to the figures. They show:

[[0006]] fig. 1: Layer stack before removal from the rigid substrate.

[[0007]] fig. 2a: A second version of the layer stack before removal from the substrate.

[[0008]] fig. 2b: Layer stack of the second version, final state.

[[0009]] fig. 3: Layer stack for {11}["superstrate configuration" before removal from the substrate.

{process-}

[Detailed Description of the Invention]

[0010] On a rigid substrate 7, consisting, e.g., of glass, ceramics or metal, a soluble intermediate layer 6 is deposited, e.g., by vacuum deposition. This soluble intermediate layer, a so called "sacrificial layer", may consist of, e.g., table salt {(NaCl)}[NaCl] or BaF_2 , both substances are soluble in water. As a solvent, water is used in due time during the process. On the substrate 7, which is covered by the soluble intermediate layer 6, a supporting layer 5 is deposited, e.g., a metal layer by vacuum deposition or, e.g., a spin

coated polymer layer, like e.g., a commercially available temperature resistant plastic with the name "Kapton".

[[0011]] On the supporting layer 5 a sequence of layers 1-4, a so called layer stack 10, is deposited, the layer stack employing semiconductors as electrically active layers which contain the electronically and optically necessary layers for the solar cell. All layers are applied on a rigid substrate during the processing employing deposition or other techniques.

[[0012]] The further processing steps are described using as an example a

~~{CuIn_xGa_ySe_z}~~ **[CuIn_xGa_ySe_z]** with $x, y, z \geq 0$ (called CIGS for the following) solar cell, the description may be employed in a similar way to other types of cells as, e.g., CdTe.

For the CIGS cell, the further steps essentially correspond to the already known methods (H.W. Schock and A. Shah, "Status and prospects of photovoltaic thin film technologies", Proc. ~~{14th}~~ **[14th]** European Photovoltaic Energy Conference, Barcelona, Spain, 1997, H.S. Stephens & Associates, UK, 1997, pp. 2000-2005): Onto the supporting layer 5 the back contact 4 consisting of, e.g., sputtered Mo is deposited. With the known techniques, -e.g., simultaneous or sequential vacuum deposition of the elements Cu, In, Ga and Se the CIGS compound consists of-, the absorber layer 1 with a few micrometer thickness is formed, here, the known techniques, e.g., by grading the composition of the layer, may be applied to obtain an as high as possible efficiency of the finished cell. The temperature of the sample during deposition is about, e.g., ~~{400°C.}~~ **[400°C.]** At this ~~{temperature.}~~ **[temperature,]** a suitable polymer supporting layer as described above still remains intact, but cells with high efficiencies are obtainable. In the ~~{manufacturing}~~ **[manufacturing]** step, in addition, some Na in a suitable form and/or compound may be added, since it is known that addition of Na has a positive effect on the characteristics of the finished cell.

The Na addition may be avoided, e.g., if Na is delivered from the intermediate layer, if this layer contains Na, in a suitable amount and form. After this, the window layer 2, consisting of, e.g., ZnO, CdS or ZnSe, and the front contact 3 consisting of, e.g., ITO (indium-tin-oxide) is deposited; depending on the method used, still further differentiating like, e.g. deposition of CdS, or doping the outer part of the window layer in order that this part is suitable as a front contact may be of use. Depending on the lateral size and the structure, individual solar cells are delineated by, e.g., scribing or {}the outer part of the window layer in order that this part is suitable as a front contact may be of use. Depending on the lateral size and the structure, individual solar cells are delineated by, e.g., scribing or photolithography, and, eventually, antireflection and mechanical protection layers (e.g., an additional optically transparent and UV-resistant polymer film) deposited.

[[0013]] At this stage of the manufacturing sequence, the intermediate layer 6 may typically be dissolved, separating the substrate 7 from the supporting layer 5 with its thereon applied layer stack 10. The supporting layer 5 and the layer stack 10 form the solar cell, which is now flexible. If the intermediate layer 6 consists of, e.g., NaCl or BaF₂, water may be used as a solvent. For intermediate layers which are insoluble in water, or due to other reasons, other solvents may be used.

[[0014]] With this method according to the invention, e.g., a CIGS solar cell with 12.8% efficiency on a polyimide substrate was obtained. The thickness of the spun-on polyimide was about 20 {}[μm], the thickness of the essential layers needed for proper electrical-optical functionality below 4 {}[μm]. The whole structure is flexible and can be employed for the already described applications.

[[0015]] This procedure has several advantages as compared to known manufacturing methods: Fabrication of such stacks of layers is easier and more reproducible in most cases if they are deposited on rigid substrates, e.g., the optimal deposition temperature to get high efficiency can be controlled easier. In addition, the thin substrate foil is never exposed to conditions which might be detrimental to the unprotected nude foil like high temperature and/or mechanical stress. In addition, due to mechanical stress inhomogeneities in the foils, faults and inhomogeneities in the grown layers may lead to catastrophic electrical shorts.

[[0016]] The rigid substrate 7 may be reused after removal of the layer-structure {11} [11].

{11}

[[0017]] It is therefore essential for the solar cell according to the invention that the cell is formed on a rigid substrate during most of the fabrication steps, the cell then being removed from the rigid substrate, and being flexible afterwards. It may be used in its flexible condition, or again joined with a further rigid substrate.

~~{High quality thin film solar cells which consist in most cases of polycrystalline compound}~~

[[0018] **High quality thin film solar cells which consist in most cases of polycrystalline compound**] semiconductors like, e.g., ~~{CuIn_xGa_ySe_z}~~ [CuIn_xGa_ySe_z] with $x, y, z \geq 0$ (often abbreviated as CIGS) presently have high efficiencies (12%-18%), they are comparable to those of conventional single crystal silicon solar cells. The layers needed to fabricate the cells are grown on rigid glass substrates in most cases. The thickness of the

electrically essential layers is a few micrometer only, the material needed to fabricate one square meter of solar cell is only a few grams. If fabricated in large volume, fabrication costs therefore will be much lower compared to those of conventional crystalline silicon cells.

[[0019]] For some applications, it is ~~{advantagous}~~ **[advantageous]** if the whole solar cell structure remains flexible. E.g., in order to avoid relatively expensive glass substrates, to place the cells on curved surfaces like facades, tiles, or curved casings of electrical consumer products, or simply to save weight, the latter being particularly essential for space applications. In addition, a large area ~~{strcture}~~ **[structure]** may be simply rolled for transportation. But for small area applications, too, flexible solar cells are of interest, e.g., as an energy source for pocket calculators or "smart cards" which may contain electronic circuits and displays, but still have to be flexible to some extent.

[[0020]] Figs. 2a and 2b show variations of the fabrication method according to the invention. Fig. 2a shows a second layer stack before dissolution from the substrate. Here, for fabrication, the intermediate layer 6 is deposited on the substrate 7 as already described. However, no supporting layer 5 is applied at the present stage, but the deposition of the further layers 1-4 of the solar cell structure follows: as already described, e.g., backcontact 4 (e.g., Mo) followed by CIGS 1, which may eventually be supplied with some Na, window layer 2 and front contact 3. The transparent polymer 5 is now put onto the structure as a supporting layer 5, and the whole structure ~~{H}~~ **[11]** is separated from the rigid substrate 7 by dissolving the intermediate layer 6. With this variant, the deposition temperature may even be higher than ~~{400°C}~~ **[400°C]**, since the polymer layer is

deposited afterwards; in addition, instead of a polymer, a plastic with less good temperature stability may be employed.

[[0021]] Fig. 2b shows a second layer stack in the final state. Discernible are the layer structure ~~{H}~~ [11] as described in Fig. 2a and a further layer 8, e.g., a plastic which may be attached as a protection layer.

~~{An additional variant is to remove the layer stack carefully from the rigid substrate before}~~

[[0022] **An additional variant is to remove the layer stack carefully from the rigid substrate before]** depositing the top polyimide layer, and put it afterwards on a transparent foil, this eventually employing a transport temporary substrate. In both cases, an additional protection layer which also may be of use for the mechanical stability may than be attached to the bottom side, i.e. on the back-contact layer, by proper glueing or using other methods. The flexible composite may, for certain applications, again be joined with a rigid substrate. E.g., for conventional CIGS cells, glass substrates in the "substrate structure" are employed. For the complete encapsulation, therefore, two glass plates are needed, mainly a second plate for mechanical and chemical protection and through which the light penetrates. Using the solar cell according to the invention, the bottom glass plate is superfluous, therefore one glass plate may be saved, such an arrangement is reasonable in such harsh and corrosive environments where transparent plastic coverages yield insufficient protection.

[[0023]] The two methods described above correspond to, as described in the corresponding technical literature, the "substrate configuration"; i.e. the substrate glass plate of the conventional rigid cells is not crossed by the light. In the "superstrate

configuration", which again is described in the technical literature, light impings through the glass substrate; using the conventional manufacturing sequence, the transparent front contact is deposited first onto the glass substrate, followed by the window layer and the other layers. E.g., for CdTe thin film solar cells on glass substrates, this configuration is mainly employed.

[[0024]] The present invention may be employed for the "superstrate configuration", too.

[[0025]] Fig. 3 shows a layer stack in the "superstrate configuration" before dissolution from the rigid substrate. On the substrate 7, the intermediate layer 6 and supporting layer 5, the transparent front contact 3, the window layer 2, the absorber layer ~~{H}~~ [1] and the back contact 4 follow. The manufacturing steps are performed analogously.

[[0026]] As an intermediate layer, a large class of materials is possible. Many alkali-halogenides including NaCl, NaF, KCl are suited and, in addition, easily soluble in water, the same is true for ~~{Ha-}~~ [IIa-]fluorides like ~~{BaF₂-As}~~ [BaF₂, As] further suitable materials all those may be considered which are sufficiently temperature resistant and for which a solvent exists which may be employed in the corresponding environment without compromising the functionality of the layer structure.

[[0027]] Special consideration has to be given to the quality of the layers and especially to their adherence and possible delamination phenomenons. The structures mentioned as examples in the invention have proved also in the practical realization that, in incomplete enumeration, the Mo layer on polyimide can be used as a contact layer, the NaCl intermediate layer does not ~~{impede the}~~ [impede the] adherence or the further fabrication, the special spun-on polyimide layer withstands the temperatures during the fabrication and maintains the mechanical and optical properties required.

[[0028]] The layers used for the formation of the proper solar cell may include different classes of materials, too. Polycrystalline compound semiconductors like CuInGaSeS belong to such a class. With this notation $\{CuIn_yGa_zSe_wS_u\}$ $[CuIn_yGa_zSe_wS_u]$ is meant, where the parameters y, z, w and u may have any non-negative value, but, as known, with the values limited to special smaller ranges for optimal cells. This family of materials spans therefore compound semiconductor layers of the I- $\{E\}$ $[III]$ -VI system of the chemical periodic system, in particular, they include (the parameters y, z, w, u are ~~non-itted~~ **[omitted]** in the following) CuInSe, CuInGaSe, CuGaSe, CuInS, CuInGaSSe, further materials may be used, too.

[[0029]] From the $\{H\}$ $[II]$ -VI family of the chemical periodic system, CdTe as well as further compounds can be employed. Likewise, compounds from the $\{E\}$ $[III]$ -V family of the chemical periodic system like GaAs, or group IV semiconductors of the chemical periodic system like Si or Ge may be employed.

[[0030]] All these compounds appear in the solar cell according to the invention in most cases in the form of polycrystalline layers. However, the structure of the layers may be polycrystalline, microcrystalline, nanocrystalline, micromorph or amorphous, too, as are the names for the different structures according to the technical literature.

[[0031]] In addition, instead of depositing a sequence of layers for formation of a single solar cell,- such a sequence contains at least one absorber layer and one window layer as well as contact layers-, several such layer sequences may be deposited successively. If two such sequences are employed, e.g., a "tandem cell" is formed where the light first passes the cell structure with the higher band gap, then the structure with the lower band gap, with this arrangement, the efficiency can be increased. Structures with more than two such

sequences for formation of triple cells, or multiple cells with even more such single solar cells are possible, too.

[[0032]] The partially transparent electrical contact 3 consists, e.g., of the semiconductor indium-tin oxide (ITO) or ZnO or of a combination of such layers, the back contact 4 may consist of a metal or a semiconductor or of both, as is known.